SPINEL FORMATION IN AN IMPACT PLUME: A THERMODYNAMIC APPROACH. D. Siret and E. Robin. Laboratoire des Sciences du Climat et de l'Environnement, C.E.A./ C.N.R.S. 91198 Gif-sur-Yvette cedex, France.

Introduction. Nickel-rich spinel is recognized as a cosmic event marker [1-3,5]. Spinel is found in K/T boundary sections all over the world [1-3,14], in lower-middle Jurassic hardground [13], in late Pliocene sediments [4] and in upper Eocene sediments [12]. Its composition is characterized by a high nickel oxide concentration (NiO>1 wt%) and a high iron oxidation state (Fe^{3+}/Fe_{tot}>70 mole%) involving formation in an oxygen-rich environment [9]. Robin et al. [5] have shown that oxidation of meteoroids and impact generated products in the atmosphere leads to the formation of Ni-rich spinel. Direct condensation from a gas phase [3] or crystallization from a high temperature melt [1,2,7] generated by a meteorite impact have also been suggested as potential sources for Ni-rich spinel. However, there is to date no compelling evidence of spinel condensation/crystallization from an impact plume.

Meteorite impacts produce high temperature and pressure plumes that rapidly expand. During this stage, temperature and pressure decrease allowing condensation reactions to occur. As these conditions are not reproducible experimentally, the only way to determine the condensation sequence is thermodynamic modeling. We report here the first numerical simulation performed on the physical and chemical reactions that occur in an impact plume, depending on temperature and pressure conditions. The purpose of this study is to determine whether the plume can provide the kind of environment (temperature, pressure, oxygen fugacity) needed for the formation of Ni-rich spinel.

Method of calculation. Two projectile compositions have been considered: first, an ordinary chondrite (OC) and second, a carbonaceous chondrite (CI) [1]. Calculations have been performed between 6000 K and the solidus. Indeed, there is no thermodynamic data above 6000K. Pressure have been considered between 500 bar and 10^{-9} bar.

Thermodynamic calculations have been performed using GEMINI2 code, that allow to determine the equilibrium states in complex chemical systems by minimization of Gibbs energy, from atomic balance and (T,P) conditions. Thermodynamic equilibrium between gases and condensates is assumed during the whole cooling. 15 elements (H, C, N, O, Na, Mg, Al, Si, S, K, Ca, Ti, Cr, Fe, Ni), 311 pure substances, 202 gases, and 12 ideal solutions listed below have been considered.

- 2 liquid solutions (binary and/or ternary interactions are considered except for Na, K, and Ti):
  - Oxide: Na_2O, MgO, Al_2O_3, SiO_2, K_2O, CaO, TiO_2, Cr_2O_3, FeO, Fe_2O_3, NiO and associated dissolved metal
  - Metal: Na, Mg, Al, Si, K, Ca, Ti, Cr, Fe, Ni and associated dissolved oxide;

- 10 solid solutions (no binary or ternary interactions considered) :
  - Spinel: AB_2O_4 structure where A: Mg^{2+}, Fe^{2+}, Ni^{2+} and B: Al^{3+}, Ti^{4+}, Cr^{3+}, Fe^{3+},
  - Olivine : $(Ca,Fe,Mg,Ni)_2SiO_4$,
  - Feldspar: $Al_2CaSi_2O_8$ – $AlKSi_3O_8$ – $AlNaSi_3O_8$
  - Melilite: $Al_2Ca_2SiO_7$ - $Ca_2MgSi_2O_7$
  - 3 oxide alloys: MgO-CaO-FeO-NiO
  - 3 metal alloys: Cr-Fe-Ni, Al-Si-Cr-Fe-Ni (BCC), Al-Si-Cr-Fe-Ni (FCC).

Results and discussion.

Impact plume without atmospheric interaction. Calculations show that spinel does not condense from the gas phase. Thus, the assumption of direct spinel condensation from an impact vapor plume can be excluded [3]. However, spinel crystallizes from a liquid phase condensed at high temperature in the plume but its composition is reduced (Fe^{3+}/Fe_{tot}<55 mole% and NiO<0.6 wt%). These results agree with those enounced previously [9,17] attesting that an impact plume composed of projectile material only represents a too reducing environment to allow Ni-rich spinel formation. Gayraud et al. envisaged an external source for oxygen, as H_2O dissociation but even in the case of carbonaceous chondrite, containing 17 wt% water, the oxidation remains unsufficient. Different mixtures of target and projectile material have also been studied and no one provides the kind of environment needed. Thus, the hypothesis of Ni-rich spinel formation in an impact plume without atmospheric interaction can be excluded.

Impact plume with atmospheric interaction. The model still predicts that spinel does not condense directly from the gas phase but crystallizes in a liquid condensed at high temperature. Highly oxidized spinel enriched in nickel oxide (Fe^{3+}/Fe_{tot}=70-96 mole% and NiO=4-14 wt%) appears between 1600K and the solidus, for an oxygen fugacity $fO_2>10^{-5}$ bar. Calculated spinel composition and oxygen fugacities well agree with those measured in laboratory experiments but the temperature of first appearance is lowered by 200°C [9]. Such a discrepancy may be due to the fact that we have considered ideal spinel solution. However, starting with chondritic material, it has not been possible to reproduce the wide range of Al_2O_3 and Cr_2O_3 contents in spinel composition observed in the sediments associated to the K/T boundary [2,11] suggesting that the K/T spinel crystallized from a liquid of non-chondritic composition.

Conclusions. Thermodynamic calculations of the condensation sequences that occur in a plume generated by meteorite impact show that:

1) Spinel never condenses directly from a gas phase but crystallizes from a liquid that may condense at high temperature or result from the oxidation of meteoritic debris in the atmosphere.
2) Crystallization of Ni-rich spinel requires an interaction between the plume and the atmosphere.
3) The Ni-rich spinel observed in the K/T boundary sections does not form from a chondritic liquid. We suggest some chemical fractionation of the liquid phase from which K/T spinel crystallized. Whether such a fractionation results from condensation in the plume or atmospheric ablation of impact debris is still questionable.

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